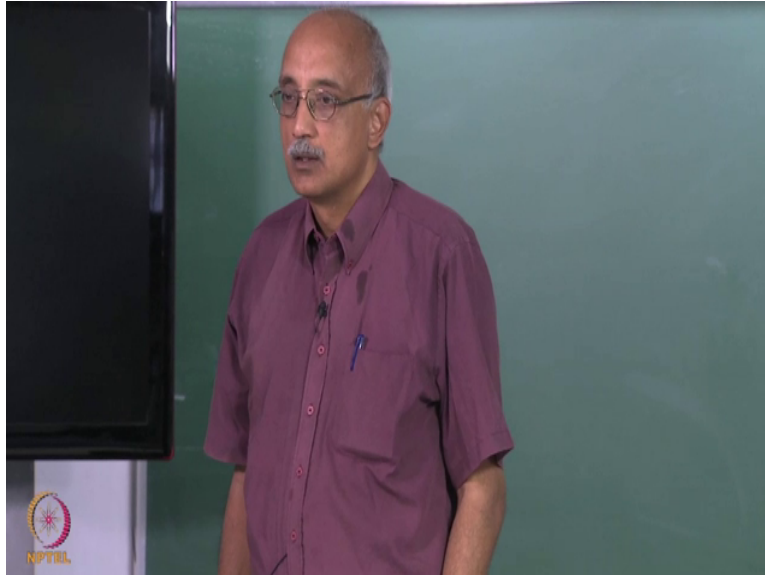**Chemical Engineering Principle of C V D Processes**
Professor R. Nagrajan
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Indian Institute of Technology Madras
Lecture No 15
C V D Transport Phenomena: Conservation Equations

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Good morning and welcome to the next lecture in our course on Chemical Engineering principles of C V D processes. I had circulated some links for lectures that are in the N P T E L course on Advanced Transport Phenomena. So I hope that you had a chance to look at these lectures.
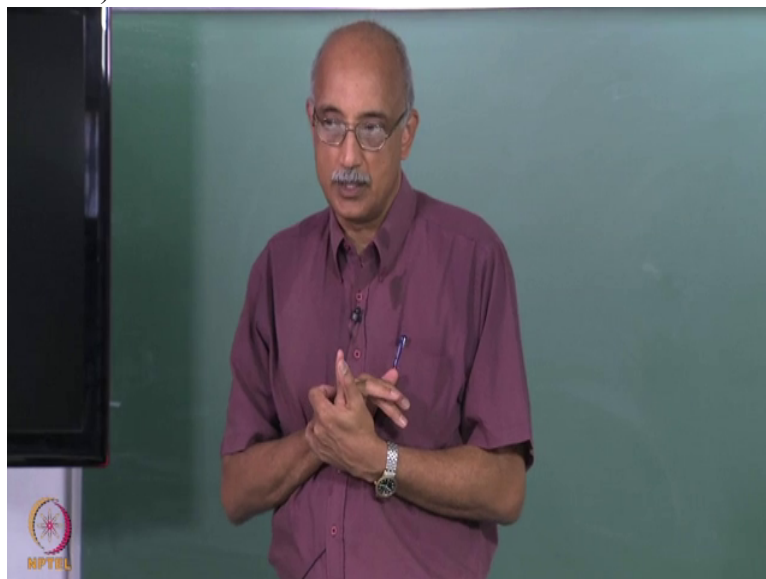
There was one lecture on the C V D process involved in deposition of tungsten on bulb walls and the other one was on the hot corrosion process. And then there were

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additional lectures on some of the fundamentals of transport phenomena which we need to understand for

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the, for the remaining portion of this course.

We are going to concentrate quite heavily on the transport aspects for the remainder of the course predominantly. Towards the end we will go back and discuss a few more applications of C V D technologies. But before we do that it is important to understand the transport phenomena that are involved.

Now in order to fully understand the transport processes in a C V D reactor you have to first understand how these transport phenomena are interlinked in a chemically reactive flow system. Because although the C V D process itself is a mass transfer process. You are taking some material from the gas phase and depositing it on a substrate in solid phase. So it is clearly, fundamentally it is a mass transfer process. But you cannot study the mass transfer process in isolation.

You have to really study it in terms of its relationship to the other prevailing transport phenomena such as momentum transfer and heat transfer and entropy conservation and so on. So it is important to get a full systematic understanding of the conservation laws. So we have mass conservation, momentum conservation, energy conservation, entropy conservation and so on which you have studied in your earlier courses.

But it is good to spend a few minutes kind of recapping and realize how they all kind of hang together. In any conservation equation there are 4 terms as we have discussed earlier. There is a net rate of change term, there is a convective term, there is a diffusive term and there is a source term. So regardless of whether you are looking at mass conservation or momentum or energy or entropy all these terms appear in the equation.

Conservation equations are those that apply to all materials. They are not specific to the fluid or system under consideration. Later on we will deal with constitutive laws which are specific for the material that is being studied or the fluid that is being studied or the system that is under analysis. So typically you start by writing the conservation equations and you use your constitutive relationships to obtain a closed system of solutions for the set of equations.

So the kind of, two kind of go together. So when we talk about conservation laws you have to first understand the assumptions involved in framing these laws. So one of the modules that I circulated has a discussion of various assumptions that are typically made when we try to describe flow systems. For example the simplest one is continuum versus the free molecular which depends on the Knudsen number.

If the Knudsen number is in excess of 1, you have to consider it as a free molecular flow. If the Knudsen number is much lower than 1, you consider it a continuum flow where the

Knudsen number of course is the ratio between essentially the distance between adjacent molecules to a characteristic dimension of the system.

The other assumption that is typically made is the incompressible versus compressible. In most flow situations the incompressible flow assumptions certainly simplifies the analysis by the requirement for incompressible flow is that density must be constant across streamlines, not with time. In fact it is important to understand that in compressible flow density at any location can change with time. However across the flowlines, the streamlines of flow the density must remain constant at any instant in time.

Another assumption is viscous versus inviscid flow which is really described by the Reynolds number. The lower the Reynolds number the more viscous the flow and higher the Reynolds number the more inviscid the flow. And of course, as the Reynolds number reaches very high, we also reach a transition between laminar and turbulent. So another way to characterize flow is laminar versus turbulent.

The other ways of describing flows are based on, for example dimensionality. Is it one dimensional or multi-dimensional? Or can we characterize it as quasi-one dimensional? So what we mean by these cases is, you know in a one dimensional flow the variations in properties primarily occurs along one direction. So you can assume that the variables are constant with respect to the other spatial dimensions whereas in a multi-dimensional flow you have to take into account variabilities across all dimensions.

Quasi one-dimensional essentially suggests that even though the variability along let us say, 2 out of 3 dimensions may not be zero as long as the variability is negligible compared to the variability in one dimension you can treat it as a quasi one dimensional flow by assuming that the property variations in the other two directions are negligible compared to the variation in the one direction.

And similarly you have steady state versus unsteady flow. If flow properties are constant with respect to time you call it steady state. If they are changing or varying with time you call it unsteady and again we can define a quasi steady state flow where properties are changing but

very, very slowly. So these are all ways of classifying flow systems and making certain assumptions about how flow occurs.

Another example will be Newtonian versus non-Newtonian, right? In a Newtonian fluid there is linear relationship between stress and strain whereas in a non-Newtonian fluid it can be highly non-linear.

And another way to discuss this is in terms of fluid mechanics versus rheology. Fluid mechanics is usually used to study Newtonian fluids and rheology is the name we give for studying the fluid mechanics of non-Newtonian fluids normally.

Another classification that is sometimes relevant is memory effects. Does the system remember what happened to it some time ago and also is there an action at a distance effect? Does the fluid at one location react to a stress put upon it at a different, remote location? So these are action at a distance effects and memory effects, can also be important in certain classes of fluids.

So the first thing we need to do, whether you are trying to analyze a C V D system or any system is go through this list of how flows can be classified and develop a set of assumptions that you can make regarding the flow. When you start your analysis, you can start with this set of assumptions. However you do need to go back at the end and validate the assumptions.

For example if you have assumed that something is one-dimensional flow but then when you actually do your calculations or your experimental measurements if you find that changes are happening in more than one dimension then you have to go back and relax your assumption and start treating the problem as two dimensional or higher order problem. Ok. So that is kind of step number 1.
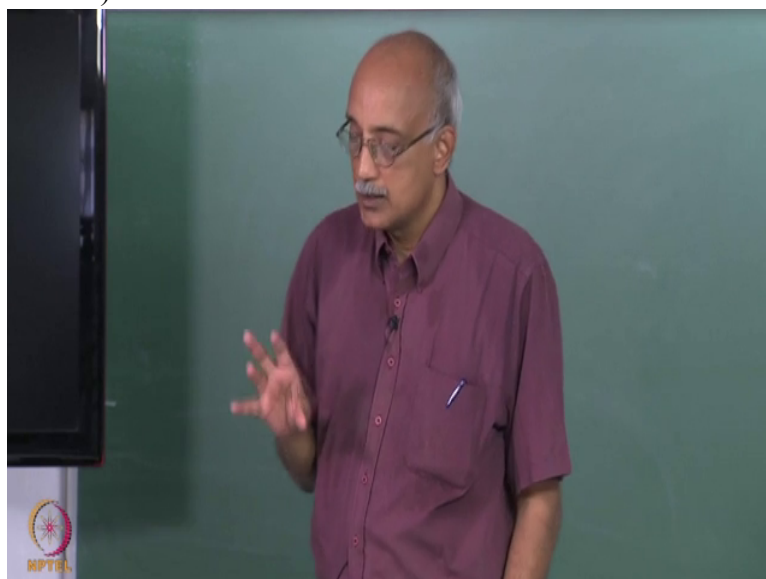
Step number 2 is to define control volumes. And a control volume is very critical in analysis

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because you essentially treat it as a system and everything outside the control volume, you treat as surroundings.

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And you try to solve your equations for the system.

So how you define the control volume can have a large bearing on how you actually approach the treatment of the problem.And there are essentially 4 types of control volumes. There is the Eulerian or fixed control volume where the control volume is fixed in space and the fluid flows through it.

The second type of control volume is called the material control volume or Lagrangian control volume in which the control volume itself moves along with the fluid flow at the same velocity as the fluid. So essentially the same parcel of fluid is contained within this control volume throughout its transit through the system.

The third type of control volume is what we call the hybrid control volume in which certain parts of the control volume are fixed and certain parts of the control volume move with the fluid. So it is a combination of the Eulerian and Lagrangian control volumes.

And finally there is the completely arbitrary control volume which is not fixed in space but which is not moving with the fluid either. It has a completely different configuration and it moves but at a different velocity vector compared to the fluid that we are treating.

So these are 4 types of control volumes and again you have to make the decision of which control volume is appropriate for the system you are studying.

For instance in a C V D reactor I would assume that you would want to use an Eulerian control volume because C V D reactor for most part is the batch system. Material comes in, reaction happens, deposit forms and the byproducts leave. So this type of system is reasonably convenient to describe with the fixed or Eulerian control volume.

However in the case where you have, for example an atmospheric pressure C V D reactor where it is essentially an open flow kind of situation you might want to consider using material control volume. Material control volume is also more appropriate when there are fairly rapid changes in the geometry of the system which makes it difficult to construct a fixed control volume which can capture all these local changes.

So there are these pluses and minuses to both approaches and you need to be aware of them as you formulate your control volumes. So you have looked at your system, made certain assumptions, you have defined your control volume.

The third step is to start writing your conservation equations, right? And when before you write the conservation equations the first thing you have to do is to define something called

the field density. Associated with each of the conserved quantities we have something called a field density parameter which is a representation of its quantity per unit volume of the fluid.
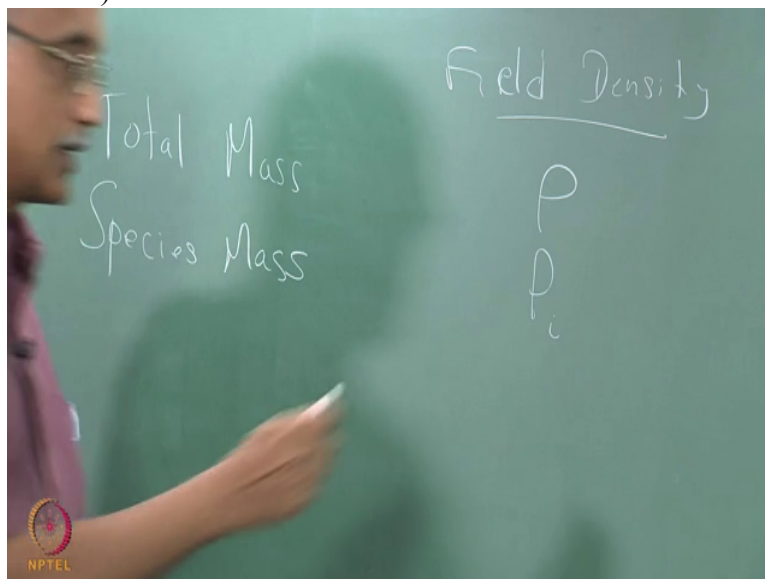
So for example when we talk about total mass conservation, the field density parameter corresponding to that is the density of the fluid itself, rho.
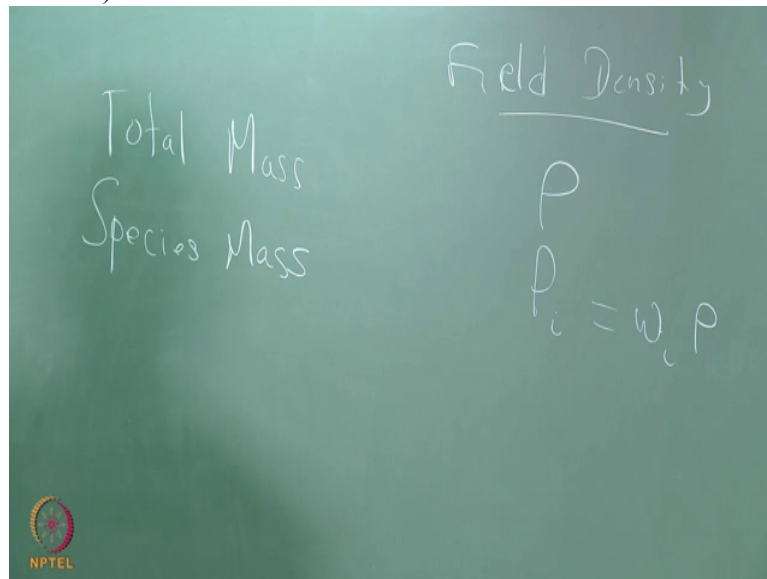
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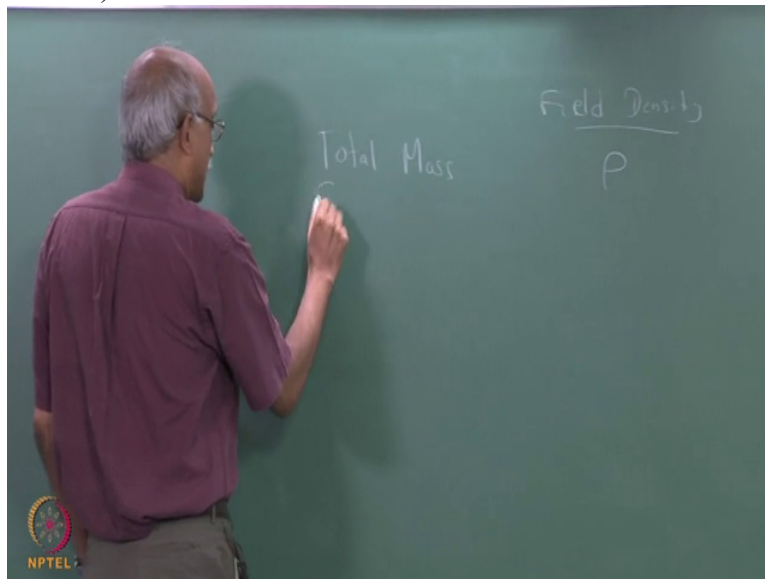
If we talk about species mass the corresponding field density parameter is rho i which you can also write as

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omega i times rho, where omega i is the mass fraction of

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species i in the mixture.

And similarly element mass is rho of k is equal to omega k rho where this is the mass fraction

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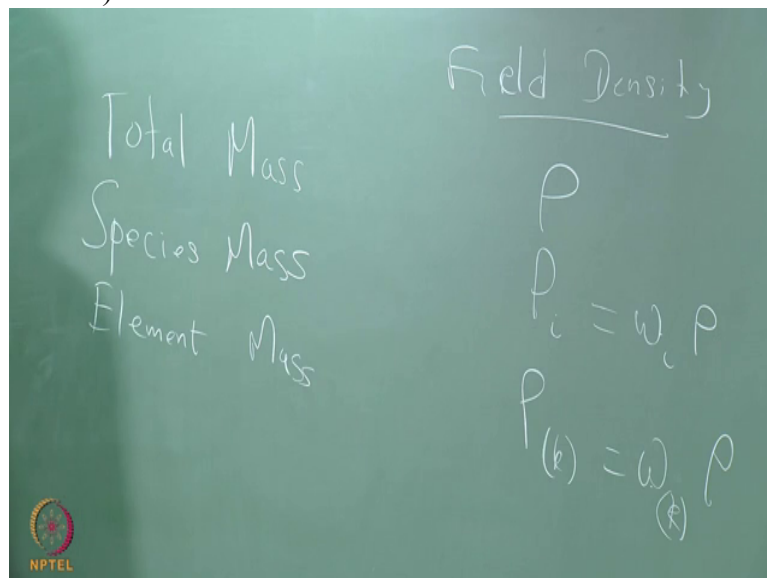
of the kth element which is estimated as omega k equals omega k i times omega i where omega k i is the mass fraction of the kth element in the ith species multiplied by omega i.

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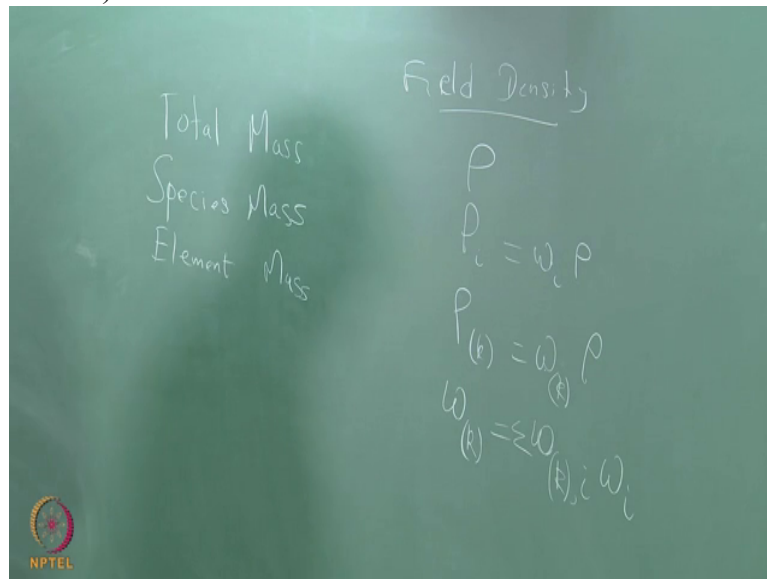
Then you have linear momentum which is another conserved quantity.

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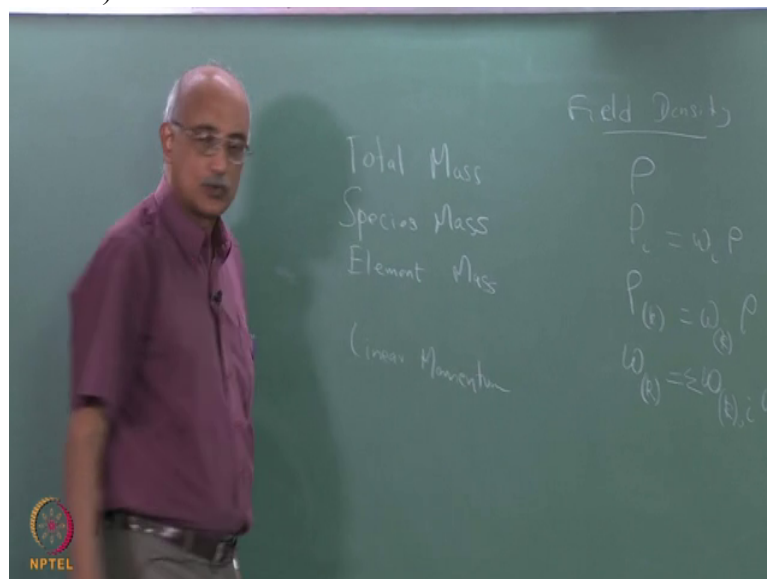
So what will be the corresponding field density parameter here, can somebody tell me? What is momentum per unit volume? How would you write it? What is momentum? m v right? So m v divided by capital V so it is rho v.

(Professor – student conversation starts)

R: Mass

M: right?

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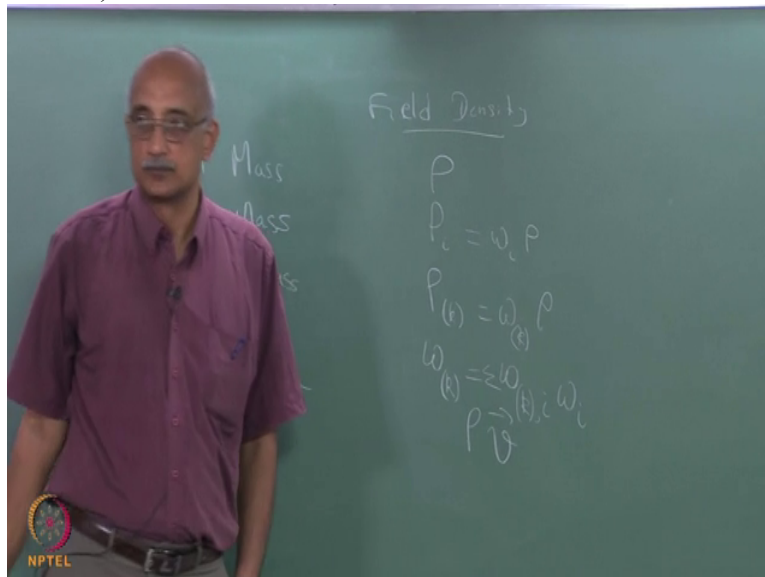
What else?

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Let us say total energy will be rho times E plus v square by two where e

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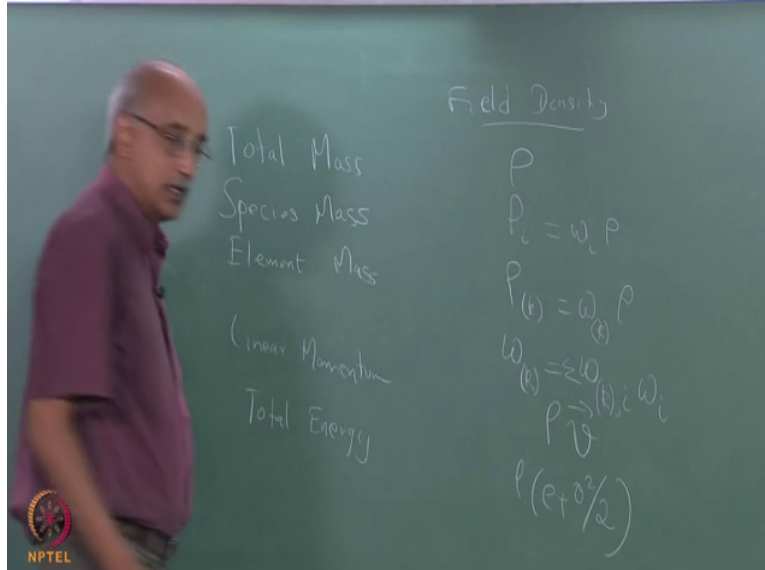
is the specific internal energy and, or rho e is the specific internal energy and rho times v squared by 2 is the specific mechanical energy. So similarly for kinetic energy you can write this as rho times v squared by 2.

Another quantity we would be interested in is entropy. And again this you can write as some rho times a specific entropy
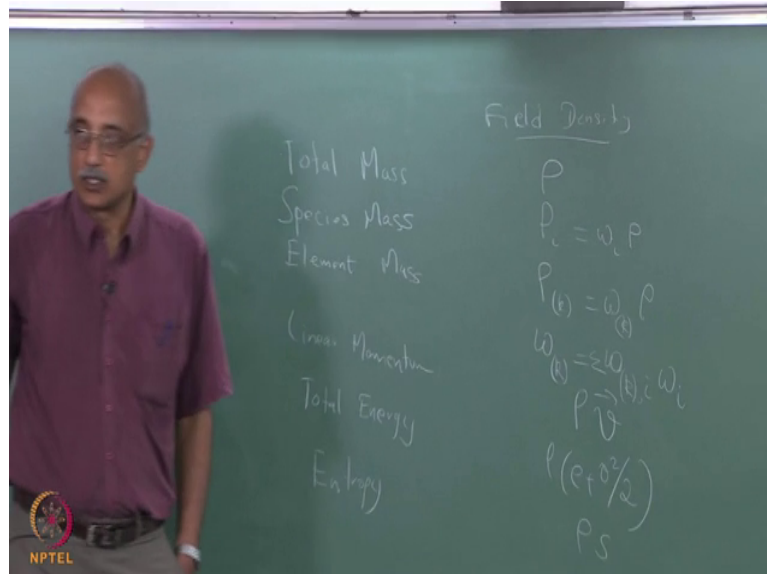
value S. So once you have defined these appropriate field density parameters it is actually quite easy to write the corresponding conservation equations.
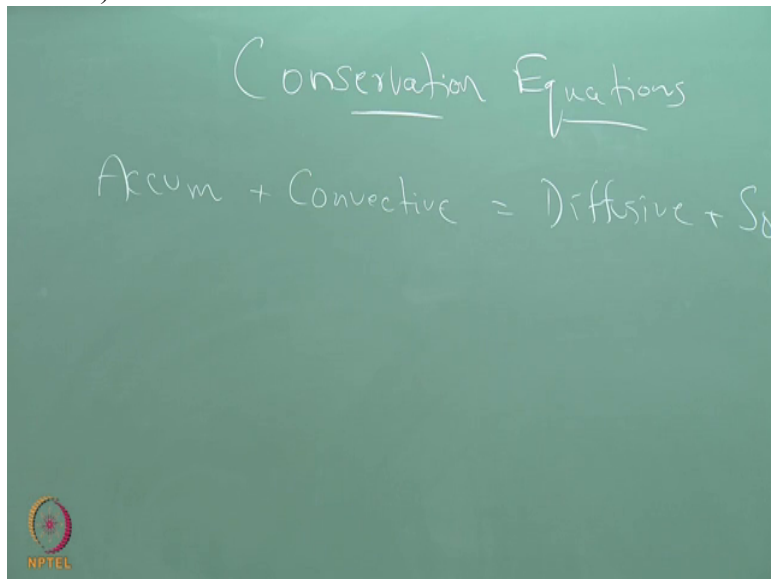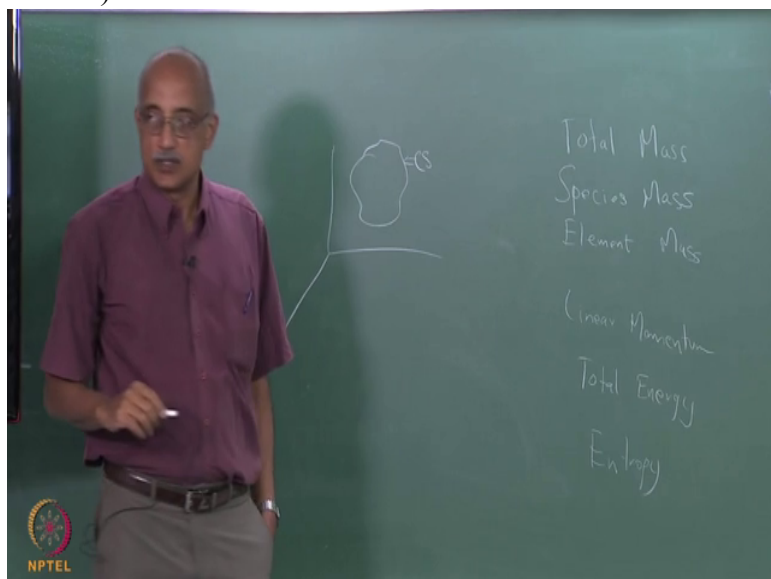
So in general,
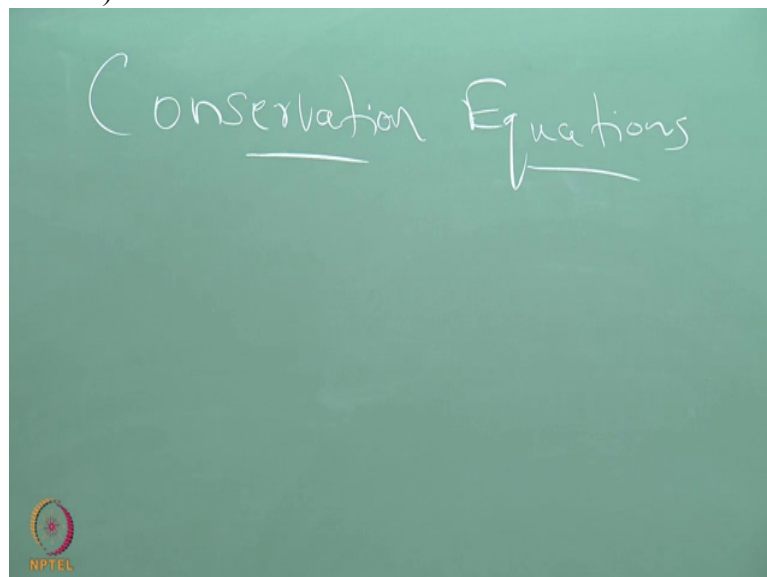
as I said the format of this equation is an accumulation term plus a convective term equals a diffusive term plus source term. And by the way when we talk about control volume's,

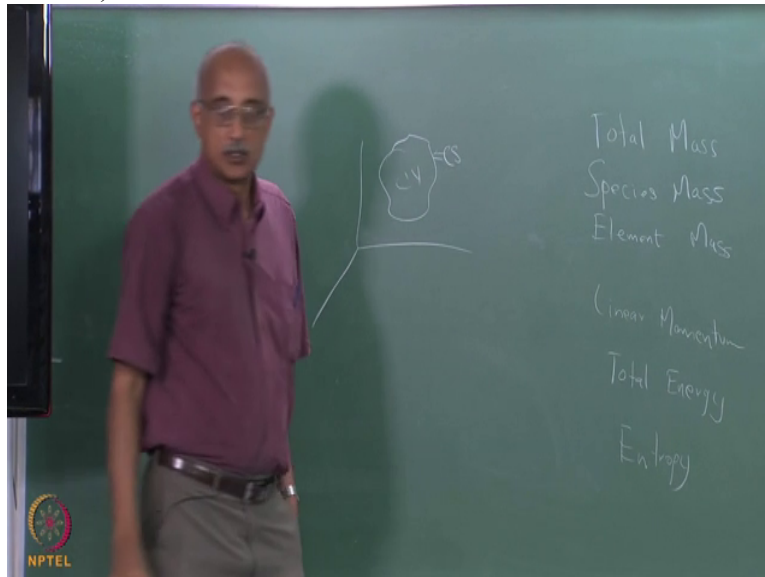(Refer Slide Time 15:25)

you know it is important to realize that, let us say that you know, this is the control surface. A control surface is

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essentially the outline or contour of your control volume in two dimensions. So what is contained within this is what
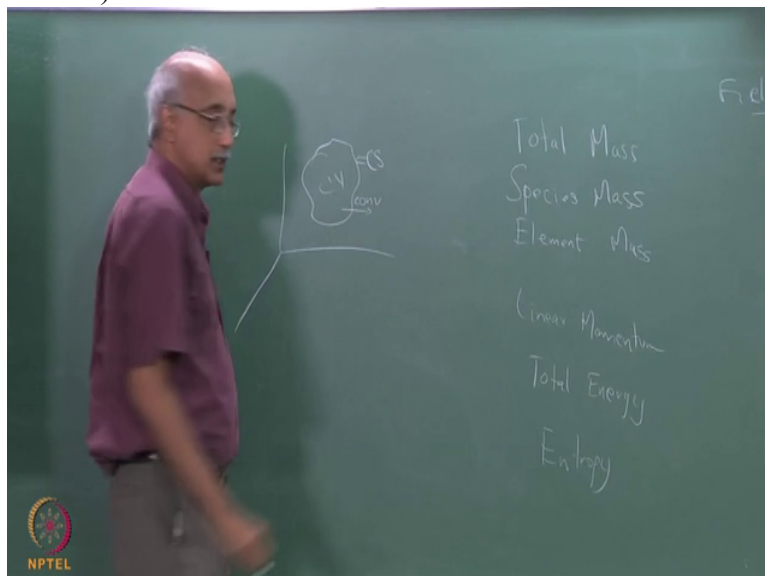
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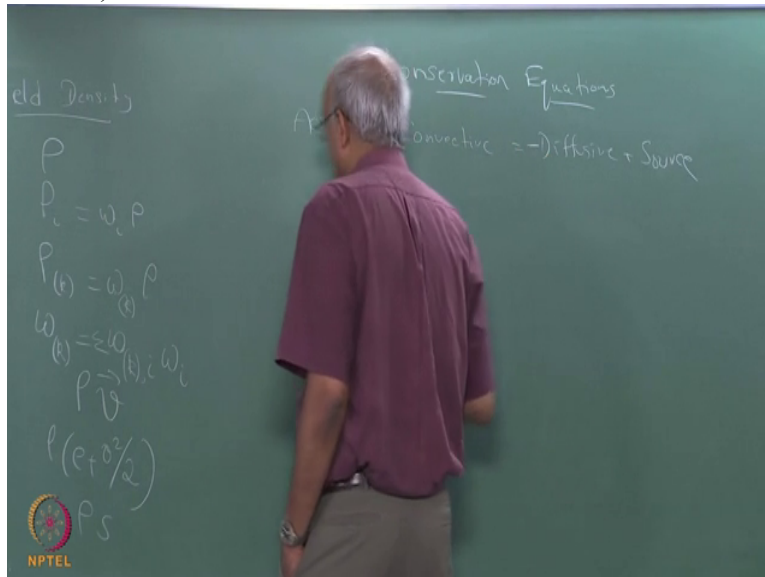
we call the control volume, right?

So by convention, when we talk about the convective term here we take it as an outflow. So convection with a positive sign

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is denoted as material leaving the system and diffusion by convention again is always, has a

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negative sign associated with it because diffusion is 0:16:15.0 as an inflow term. So convection is regarded as an outflow, diffusion is

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regarded as an inflow.

And of course when you have net consumption of the species, the source term then becomes the sink term. So the source term can also have a plus sign or a minus sign. So now that is the general equation. Now you can write conservation equations in two ways.

You can write them for integral volumes. I mean you can write the conservation equation for a, for the entire control volume in which case it will be a integral expression or you can write it for a small differential volume within the,
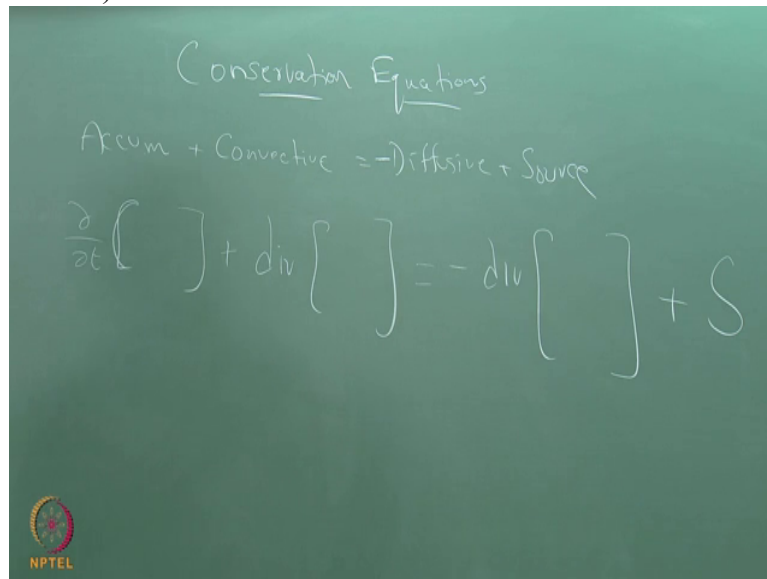
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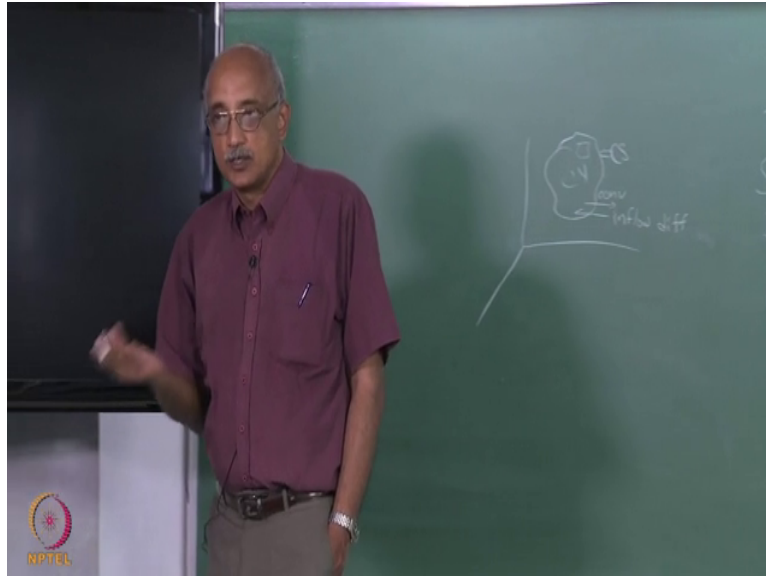
the control volume.

So you can either have an integral equation or a differential equation and typically conservation equations are written as differential equations because our methodologies for solving differential equations is fairly well-developed and also writing it as a differential equation enables us to track changes that occur within the control volume instead of treating it as a black box.

So there are certainly several advantages to treating, to solving set of equations in a differential control volume rather than a macroscopic or integral control volume. So in a, in a differential control volume this would typically have the format of del by del t of some quantity plus divergence of another quantity equals minus divergence of a quantity plus a source term which is typically written as, you know, let us call it some S and it will have units of per unit time per unit volume,

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Ok. That is the general formulation.

So you can take any conservation law and write it in this form. Now what goes in here are these field density parameters, Ok. So for total mass this would simply be del rho by del t plus divergence of rho v. So the field density parameter will go here. The field density dot v will go here and the diffusion term will have different forms for the different types of conservation equations and the source term again will have different forms for the different conservation equations.

But in general the left hand side of the equation, once you have defined the field densities then the first term is simply del by del t of the field density parameter, the second term is the divergence of the field density parameter times v, which is a vector. By the way you know what is divergence, right? Have you, now in the case of total mass, what would be on the right hand side in this conservation equation?

When you are doing mass balance, total mass balance?

It is zero plus zero. Total mass cannot diffuse and total mass cannot be created or destroyed unless you are, you have achieved light speeds or something and you are transferring mass into energy and vice versa. But under normal conditions total mass cannot be created or destroyed and total mass cannot diffuse.

Only the components of total mass can diffuse. Ok let us say, let us take this equation now, the species mass conservation equation, so this will be del rho i by del t plus divergence of rho i times v equals, now what you have on the left hand side, on the right hand side? Would you have terms?
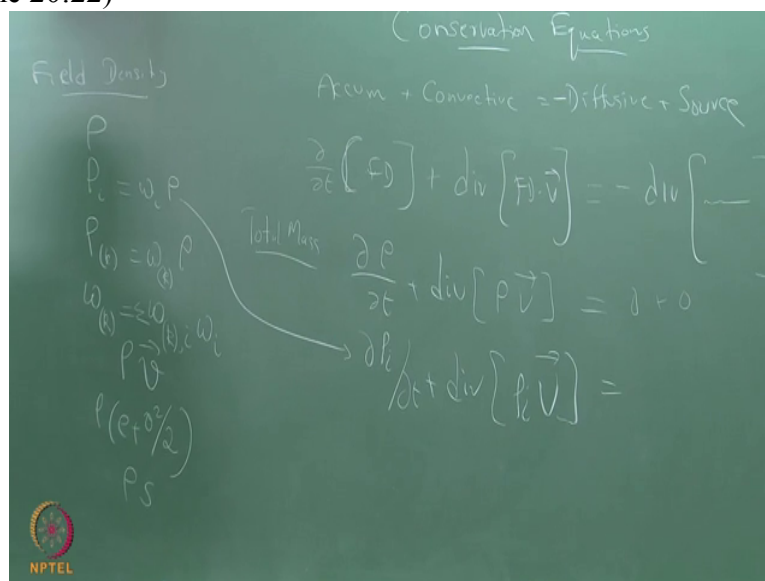
Yeah because species can diffuse and species can be created and consumed. So you will have a minus j i dot double prime which is a diffusive term plus r i dot triple prime which is the source term. Now this is what we call the diffusive flux of species i. It is a flux so this dot represents per unit time. The double prime represents per unit area.

So the diffusional conserve/ conservation, the species mass conservation equation can simply be written in this fashion. Now where do the constitutive laws apply? Where do we apply the fluid specific relationships? This and this, the diffusive flux term for species mass as well as chemical reaction term for the species involve constitutive relationships.

For example the source term requires knowledge of chemical kinetics. So you obtain that reaction rate term by applying chemical kinetic laws. And similarly the flux term, the diffusive flux term involves knowledge of flux laws.

For example in the case of species mass flux, you need to know Fick diffusion flux laws, right? So the constitutive laws are typically applied on the right hand side of the conservation equations in order to obtain the closed set of solutions.

Ok, how about element mass? How would this equation look? Again the left hand side is fairly simple; del rho k by del t plus divergence of rho k times v. Now which terms will be on the right hand side? For chemical, total mass we said

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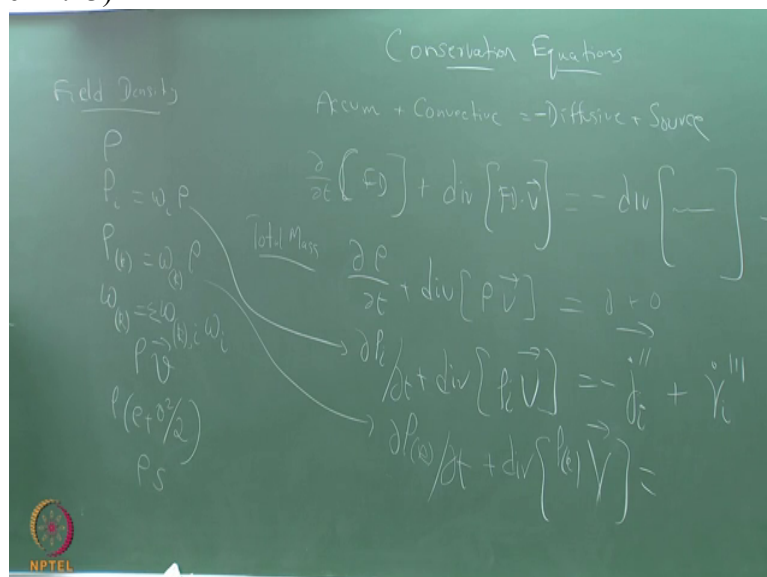
nothing on the right hand side, for species we said both the diffusive and the source terms will be there. For element mass which will be terms that appear?

Can element mass be created or destroyed? Unless it is a nuclear reaction, right? But can elements diffuse? Yeah. So only j k dot double prime term will be there. But again remember that in a C V D system, an element cannot diffuse by itself. It is somewhat of a fictitious representation.

When we talk about element fluxes it is basically a weighted sum of the fluxes of all species containing that element, right? So j k dot double prime that we have written there

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will be the summation over i of omega k i times j i dot double prime. So we take all the species diffusive fluxes, 0:23:18.8 them by the mass fractions of the elements in the corresponding species,
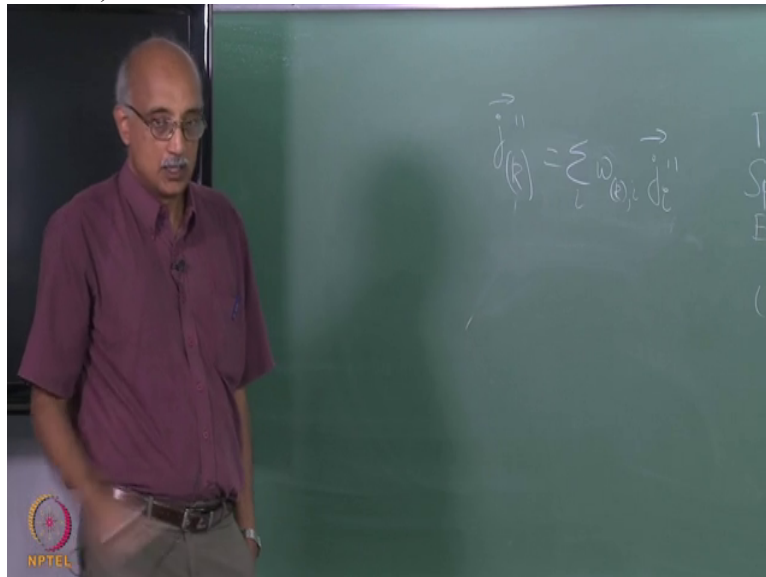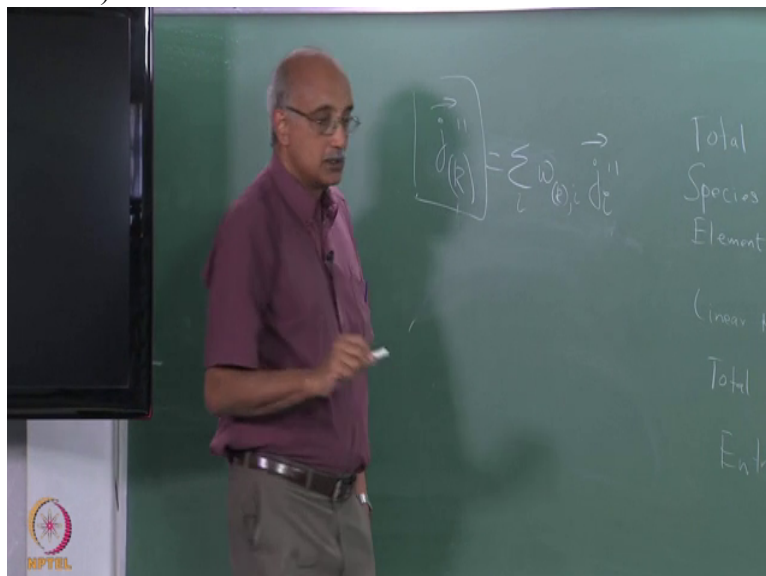
add it all up, that is what gives you the total species, total element mass flux.

And as we saw in the last few lectures when you are depositing a certain film like in a C V D reactor this is the important quantity.

Because this has to satisfy the stochiometric requirements. For example if your, the deposit has let us say, silicon and let us say there is a composite deposit of silicon tungsten carbide, right,

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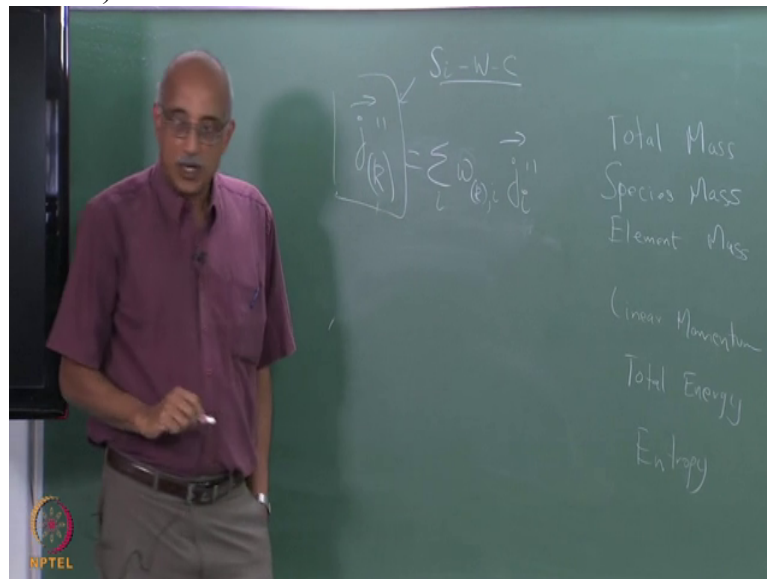
what this would mean is first you calculate the diffusive flux for S i as an element, calculate the diffusive flux of tungsten as an element, the ratio of the diffusive fluxes or the molar fluxes has to be the same as their ratio in the stochiometric compound. Otherwise you will
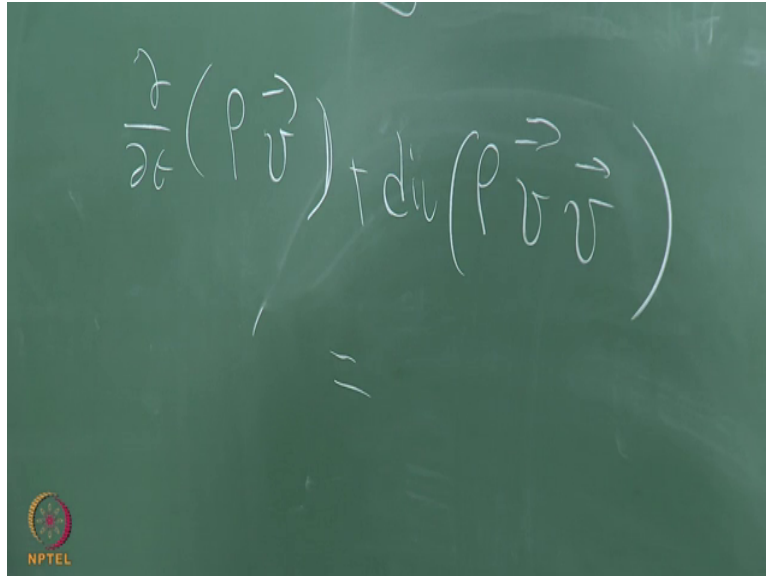
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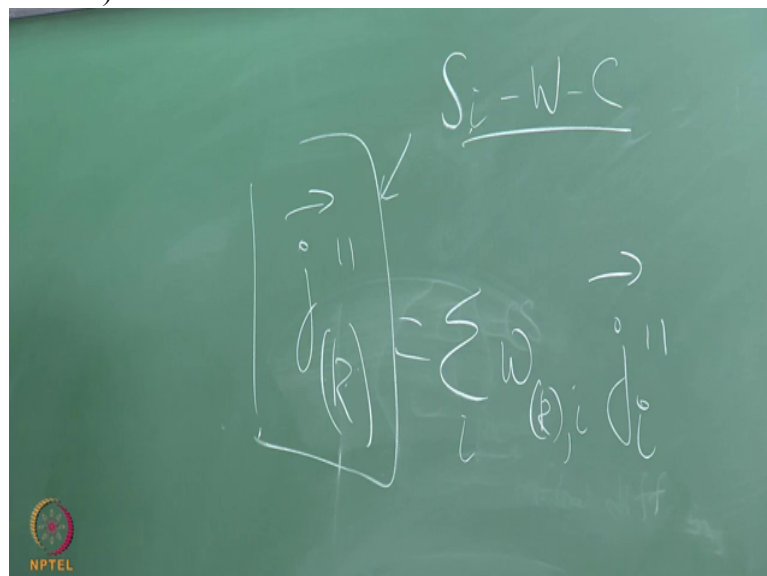
not get a stoichiometric deposit.

So the thing that we are really going to focus on mostly is how to calculate this. But to get to that point, we need to be able to do everything else. We need to be able to calculate all the other quantities that we are interested in and then home in on this particular quantity and how you calculate it and so on. Ok so let us see; let us get back to completing our discussion of conservation equations.

How do you write the, let us say the linear momentum conservation equation? So following the same format del by del t of rho v plus divergence of, in this case rho v v equals, now you have a diffusion term

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for momentum.

I mean, how, what is, how does momentum diffuse? It is clear that momentum gets convected, right? It is basically, as something flows there is a flow velocity and there is a mass, so you multiply it by two, you get momentum convection. But how, what is momentum diffusion? How does momentum diffuse? Any idea?

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In other words supposing we write minus divergence of something what should it be? And what is the source for momentum? You know there is source term.
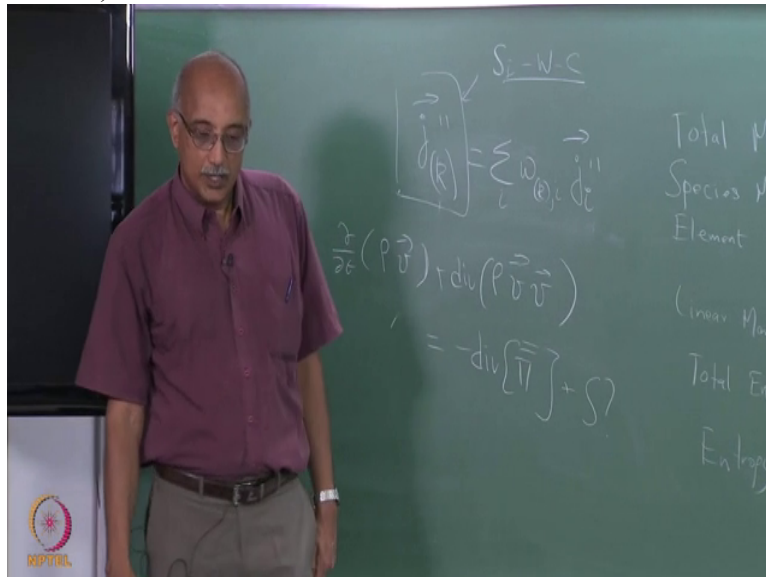
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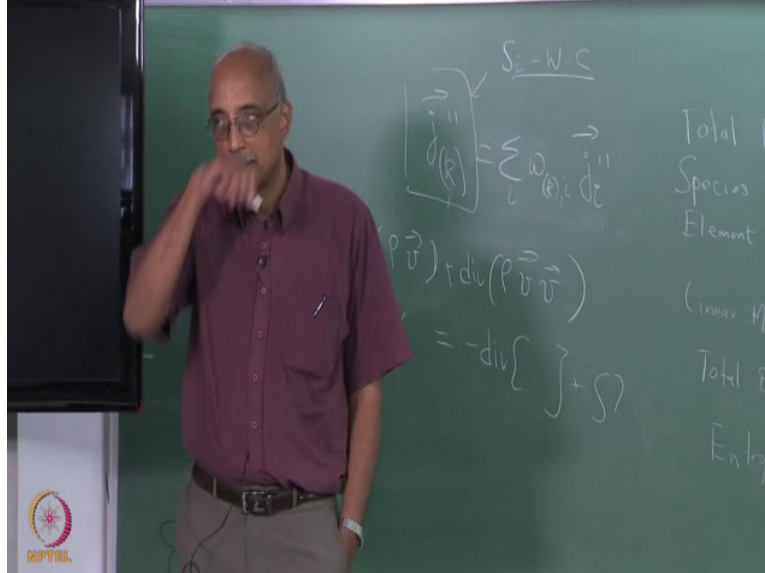
When we talk about diffusion, remember that we are talking about something that occurs around the contours or boundaries of the control volume, you know, around control surface.

So when you have momentum that is acting on this control surface, we know it can be transported in two ways. One is by convection, the other is by diffusion. So diffusion necessarily must be a surface process. So it is essentially related to surface stresses. So the term that you use here is called pi.
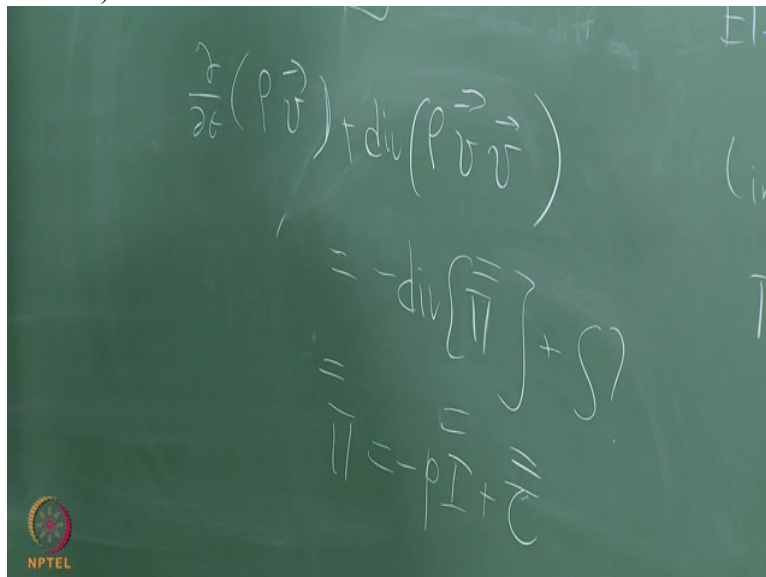
Pi is a combination

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of viscous stresses and atmospheric pressure. So you write pi as minus p times the identity vector or matrix I plus what is called an extra stress operator tau which is actually viscous stress operator.

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So that is where the viscosity term comes in.

So essentially momentum is dissipated or diffused by building up a stress along the surfaces that the momentum comes in contact with. Ok so what is the source term in this case? The source term arises because of the body forces that are acting on the species that are present in the system. So this term is given by summation over i of rho i g i.

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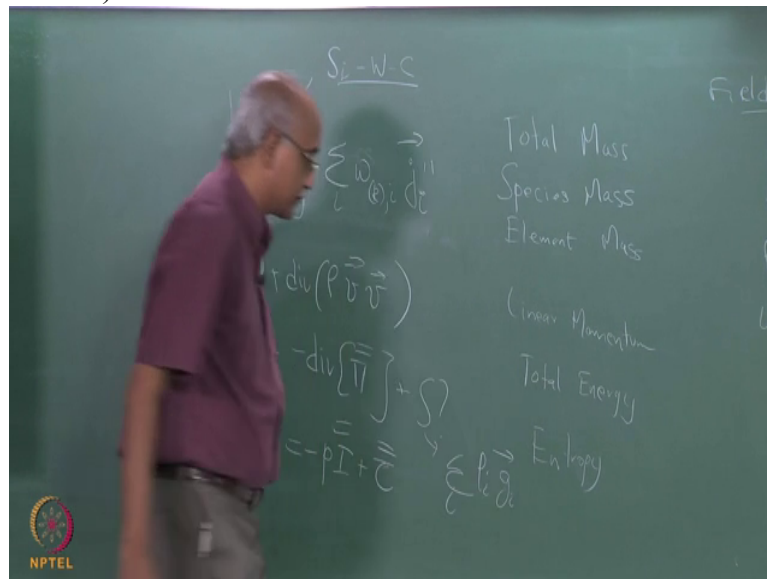
It is the summation of all the gravitational body forces that are acting on the species that are present in the system, Ok. Again I am kind of going at this at a very high level, just catching the highlights. If you want to understand a lot of this in more detail, I mean, you are certainly welcome to take my course on N P T E L Advanced Transport Phenomena which I think devotes 10 lectures to each of these, you know the mass conservation, momentum conservation, energy conservation and so on.

Or you are also welcome to read the textbook that I had given a reference for very early on Transport Phenomena/ Processes in Chemically Reacting Flow Systems by Daniel Rosner but I think for the purposes of this class, the C V D class, I think as long as you have a good overall understanding of how various quantities are conserved, in particularly we will focus more on their interaction effects later on in this course.

Ok let us talk about energy then. How would you write the conservation equation for energy?

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Again the left hand side is you know, reasonably obvious; del by del t of rho e plus v squared by 2 plus divergence of rho e plus v square by 2 times v equals, now you have to have again a diffusional term and a source term.

Now one of the diffusional terms can be written simply as minus q dot double prime which is the diffusive flux of heat and there is a volumetric heat source term which you can write as q dot triple prime, so these are essentially heat sources and heat fluxes which are present in the system.

For example this heat flux is what you would write as, you know the Fourier Law of Conduction, right? And there is another component to it as species diffuse;

there is accompanying heat diffusion that happens because of the enthalpy of the species.

So the heat flux term we will see later actually has two components to it, one is the simple molecular thermal flux and other is the heat flux associated with mass flux, right? And the q dot triple prime term is you know, it is any volumetric source of heat.

For example it could be a radiative heat that is present in the system. Or it could be because of interaction between cosmic rays and the chemical species that are present, so we try to consolidate within that term all the possible volumetric sources of heat.

Now, but what are the other terms here that we need to take into account also? For example these stresses that are developed are doing some work, right? So that has to be accounted for in your energy conservation equation.

And similarly these body forces that are giving rise to force terms are also doing work. So these two terms also have to be accounted for in your energy conservation equation. So you would then write this as plus divergence of pi dot v which is the work done by stress operators plus summation over i of rho i v times g i.

g i is not necessarily gravity. It is any

volumetric body force. Most likely it is a gravitational force but there can be situations, for example in a centrifugal reactor the body force term can be much higher than gravitational force. So these are the two extra terms that are added for the energy conservation term and what else?

Ok entropy we will write as del by del t rho S plus divergence of rho S dot v equals minus j S dot double prime plus S dot triple prime where j S double prime is again the diffusive flux term for entropy which is again associated with both mass flux as well as energy flux. They both give rise to an entropy flux as well.

And similarly the entropy source term includes all volumetric contributions to increase in entropy of the system. Now these are conservation laws that are used in transport mechanism studies. How do they relate to thermodynamics? I mean can you restate some of these equations as thermodynamic equations?

Obviously there is a relationship, you know. Energy to work conversion, how about entropy? What is the thermodynamic requirement for system entropy? It should be that the source term must be positive, right? So we can write, rewrite this equation as an inequality to say
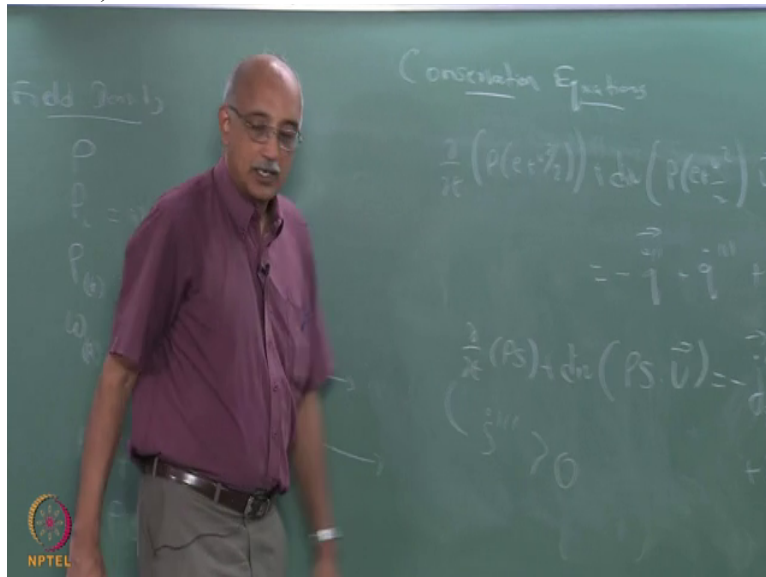
that for a system to be thermodynamically feasible the source term in entropy must be greater than zero which means that if you go back to this equation these two terms plus the diffusive flux terms, if you add them all up, it must be greater than zero.

So it is a self-consistency check, you know. When you are doing analysis of a C V D system you have to verify not only the thermodynamic validity and the transport validity but also the entropic validity to make sure that the C V D film that you are trying to achieve is feasible and will happen. If one of these three is violated, it won't happen.

So it is important to consider all modes of conservation and do a comprehensive calculation for the system as a whole. Ok so these are all the various conservation laws, again in a kind of in a nutshell and you know, you can certainly write them in different coordinate systems.

We have used Cartesian, you can use cylindrical coordinates, spherical coordinates so you know, depending on the geometry of your C V D reactor you have to restate them different ways and wherever possible, actually if you can apply an integral formulation of these equations and get away with it, fine because it is simpler to solve the integral equations than the differential equations in terms of numerical complexity and so on.

So the next thing we want to focus on is on the right hand side of the equation. You know, assume that the left hand side is something that we know either how to measure or

how to calculate. I mean you can certainly look at the time rate of change of mass by various analytical techniques; you can look at time rate of change of species mass, element mass, momentum, energy and so on.

So the left hand side of these conservation equations is not too difficult to either calculate or measure. But the right hand side of these equations is where the challenges are because they require specific information about the fluid at hand, or the material at hand or the system at hand.

For example if you want to calculate in, in energy conservation, if you want to calculate this heat flux term you have to know the thermal conductivity of the system, right? And similarly if you want to calculate momentum diffusion you have to know the viscosity that is prevailing. If you want to calculate the diffusional flux you have to know the diffusion coefficients that are prevailing.

So quantities such as mu viscosity, k thermal conductivity and D
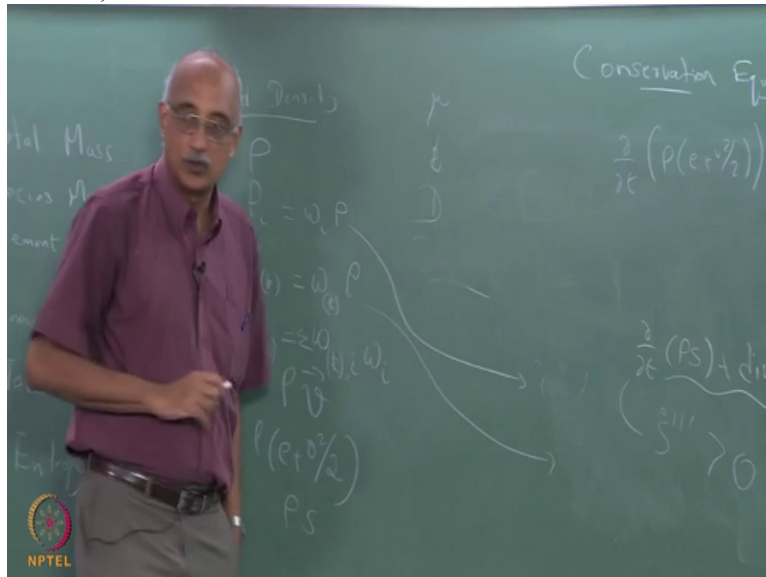
diffusivity are the very key properties that either you have to be able to estimate from the molecular properties of the system or measure based on well-designed experiments. And for these constitutive coefficients either approach is considered valid.

So the three primary types of constitutive relationships that we with are equations of state. For any fluid you have to be able to write its equation of state so that you know what its prevailing state is for a given temperature and pressure and essentially what the phase diagram looks like. What is going to be the composition of the system, what is going to be the solid fraction, liquid fraction and so on?

So the equation of state is the most fundamental constitutive relationship.

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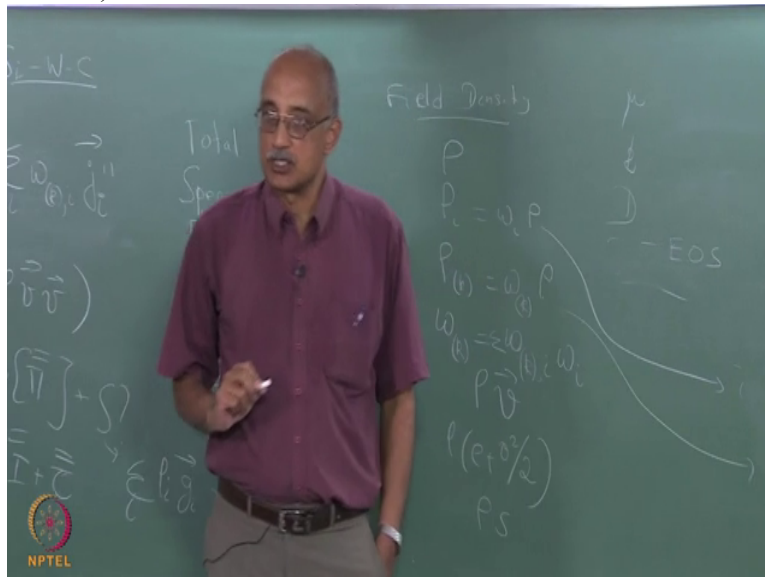
The second most fundamental, at least for chemical systems is your kinetic rate laws. Whether you assume that thermo chemical equilibrium applies or you assume that it is kinetically controlled you still need to know the corresponding rate coefficients.

So the rate coefficients themselves as well as the actual formulation of the kinetic model are also very important aspects of the constitutive relationships. And again in the C V D reactor you will realize the complexity of this because even though the overall reaction may be quite simple, you know S i H 4 going to S i plus H 2, the actual steps involved, the actual reactions involved can be many, many and to obtain the kinetic description, may be the most difficult part in closing 0:37:32.7 the C V D problem.

And then the third important constitutive relationship is the diffusion laws. How does mass diffuse,

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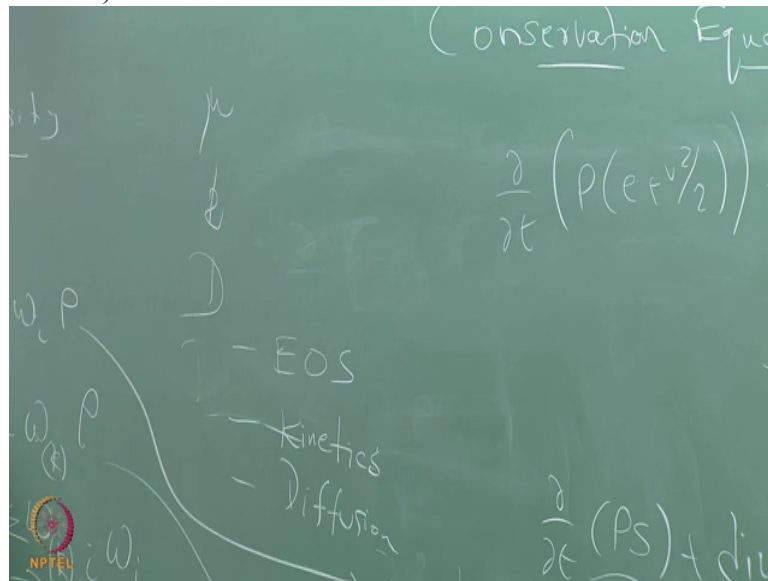
how does energy diffuse, how does momentum diffuse and so on. So without a good understanding of how to write the constitutive laws you cannot really proceed very far. It is great to be able to formulate the conservation laws, I mean it is clearly the essential step but not sufficient.

Once you have written down the conservation laws, you know, you are kind of halfway across the well, but still have to take the other step to the other side of the well. And that is to be able to write the constitutive relationships, to be able to estimate these parameters, you know. How do you estimate viscosity of a fluid or a thermal conductivity of a fluid?

Especially diffusivity is particularly complicated because every species can have a different diffusivity, right? So you have to be able to estimate diffusivities of individual chemical species that are present in the system. Some of them are dilute species and some of them are present in higher concentration and the, the equations for deriving the diffusion coefficients are very different. As the concentration of the species gets higher, the diffusion of one species can affect the diffusion of the other species.

So these types of coupling effects have to be taken into account. So in the next lecture we will spend a little bit of time particularly talking about the constitutive relationships focusing on the diffusive laws that apply for mass flux, Ok. Any questions on what we have covered today?

Ok see you.